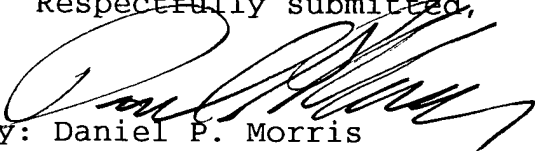September 1986."   The present application was filed within a year of this article.

     The Asahi Shinbun article reports on applicants' work and says that it has been reproduced by Professor Tanaka.   It is therefore not a proper reference, since it is essentially applicants' work.

                         Respectfully submitted,

                         By: Daniel P. Morris
                              Registration No.: 32,053
                              Tel. No. (914) 945-3217

IBM Corporation
Intellectual Property Law Dept.
P. O. Box 218
Yorktown Heights, New York 10598

/ma

S.N. 08/303,561

Appendix A

ATTACHMENT A

COPPER OXIDE SUPERCONDUCTORS

Charles P. Poole, Jr.
Timir Datta
Horacio A. Farach

with help from

M. M. Rigney
C. R. Sanders

Department of Physics and Astronomy
University of South Carolina
Columbia, South Carolina

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PREFACE

The unprecedented worldwide effort in superconductivity research that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit superconductivity above the temperature of liquid nitrogen. The time is now ripe to bring together in one place the results of this research effort so that scientists working in this field can better acquire an overall perspective, and at the same time have available in one place a collection of detailed experimental data. This volume reviews the experimental aspects of the field of oxide superconductivity with transition temperatures from 30 K to above 120 K, from the time of its discovery by Bednorz and Müller in April 1986 until a few months after the award of the Nobel Prize to them in October 1987. During this period a consistent experimental description of many of the properties of the principal superconducting compounds such as BiSrCaCuO, LaSrCuO, TlBaCaCuO, and YBaCuO has emerged. At the same time there has been a continual debate on the extent to which the BCS theory and the electron–phonon interaction mechanism apply to the new materials, and new theoretical models are periodically proposed. We discuss these matters and, when appropriate, make comparisons with transition metal and other previously known superconductors. Many of the experimental results are summarized in figures and tables.

The field of high-temperature superconductivity is still evolving, and some ideas and explanations may be changed by the time these notes appear in print. Nevertheless, it is helpful to discuss them here to give insights into work now in progress, to give coherence to the present work, and to provide guidance for future work. It is hoped that in the not too distant future the field will settle down enough to permit a more definitive monograph to be written.

The literature has been covered almost to the end of 1987, and some 1988 work has been discussed. This has been an enormous task, and we apologize for any omissions in the citing and discussion of articles.

We wish to thank the following for giving us some advanced notice about their work: R. Barrio, B. Battlogg, L. A. Boatener, G. Burns, J. Drumheller, H. Enomoto, P. K. Gallagher, R. Goldfarb, J. E. Graebner, R. L. Greene, J. Heremans, T. C. Johnson, J. K. Karamas, M. Levy, J. W. Lynn, A. Malozemoff, K. A. Müller, T. Nishino, N. Nucker, J. C. Phillips, R. M. Silver, G. Shirane, J. Stankowski, B. Stridzker, S. Tanigawa, G. A. Thomas, and W. H. Weber. We appreciate comments on the manuscript from S. Alterowitz, C. L. Chien, D. K. Finnamore, J. Goodenough, J. R. Morton, and C. Uher, and helpful discussions with J. Budnick, M. H. Cohen, M. L. Cohen, R. Creswick, S. Deb, M. Fluss, A. Freeman, D. U. Gubser, A. M. Hermann, V. Z. Kresin, H. Ledbetter, W. E. Pickett, M. Tinkham, C. E. Violet, and S. A. Wolf. Support from the University of South Carolina, the Naval Research Laboratory, and the National Science Foundation Grant ISP 80 11451 is gratefully acknowledged.

Michael A. Poole helped to develop the computer data storage techniques that were used. Jesse S. Cook is thanked for editorial comments on the manuscript. C. Almasan, S. Atkas, J. Estrada, N. Hong, O. Lopez, M. Mesa, T. Mouzghi, and T. Usher are thanked for their interest in this project.

CHARLES P. POOLE, JR.
TIMIR DATTA
HORACIO A. FARACH

Columbia, South Carolina
July 1988

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.d detailed treatment of the prop-
see the extent to which they con-
·ey agree with some of the other
.1 these two chapters.

V

PREPARATION AND CHARACTERIZATION OF SAMPLES

A. INTRODUCTION

Copper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials. Nevertheless, it should be emphasized that the preparation of these samples does involve some risks since the procedures are carried out at quite high temperatures, often in oxygen atmospheres. In addition, some of the chemicals are toxic, and in the case of thallium compounds the degree of toxicity is extremely high so ingestion, inhalation, and contact with the skin must be prevented.

The superconducting properties of the copper oxide compounds are quite sensitive to the method of preparation and annealing. Multiphase samples containing fractions with T_c above liquid nitrogen temperature (Monec) can be synthesized using rather crude techniques, but really high-grade single-phase specimens require careful attention to such factors as temperature control, oxygen content of the surrounding gas, annealing cycles, grain sizes, and pelletizing procedures. The ratio of cations in the final sample is important, but even more critical and more difficult to control is the oxygen content. However, in the case of the Bi- and Tl-based compounds, the superconducting properties are less sensitive to the oxygen content.

Figure V-1 illustrates how preparation conditions can influence superconducting properties. It shows how the calcination temperature, the annealing time, and the quenching conditions affect the resistivity drop at T_c of a BiSrCa-CuO pellet, a related copper-enriched specimen, and an aluminum-doped coun-
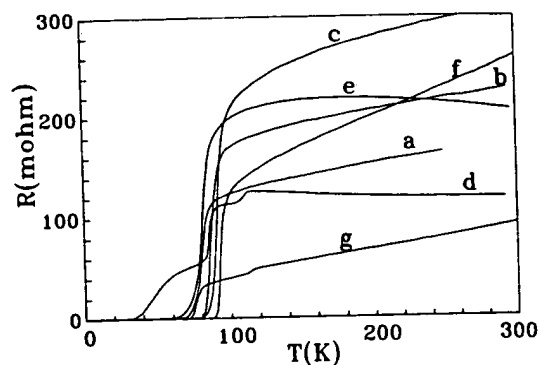
Fig. V-1. Effects of heat treatments on the resistivity transition of $BiSrCaCuO_{7-\delta}$ (a) calcined at 860°C, (b) calcined at 885°C, (c) calcined at 901°C, (d) aluminum-doped sample calcined at 875°C, prolonged annealing, (e) copper-rich sample calcined at 860°C, (f) aluminum-doped sample calcined at 885°C, slow quenching and (g) calcined at 885°C, prolonged annealing, and slow quenching (Chuz5).

terpart (Chuz5). These samples were all calcined and annealed in the same temperature range and air-quenched to room temperature.

Polycrystalline samples are the easiest to prepare, and much of the early work was carried out with them. Of greater significance is work carried out with thin films and single crystals, and these require more specialized preparation techniques. More and more of the recent work has been done with such samples.

Many authors have provided sample preparation information, and others have detailed heat treatments and oxygen control. Some representative techniques will be discussed.

The beginning of this chapter will treat methods of preparing bulk superconducting samples in general, and then samples of special types such as thin films and single crystals. The remainder of the chapter will discuss ways of checking the composition and quality of the samples. The thermodynamic or subsolidus phase diagram of the ternary Y–Ba–Cu oxide system illustrated in Fig. V-2 contains several stable stoichiometric compounds such as the end-point oxides Y_2O_3, BaO, and CuO at the apices, the binary oxides stable at 950°, (Ba_3CuO_4), Ba_2CuO_3, $BaCuO_2$, $Y_2Cu_2O_5$, $Y_4Ba_3O_9$, Y_2BaO_4, and $(Y_2Ba_4O_7)$, along the edges, and ternary oxides such as $(YBa_3Cu_2O_7)$, the semiconducting green phase Y_2BaCuO_5, and the superconducting black solid $YBa_2Cu_3O_{7-\delta}$ in the interior (Beye2, Bour3, Capo1, Eagl1, Frase, Hosoy, Jone1, Kaise, Kurth, Kuzz, Leez3, Lian1, Mali1, Schni, Schn1, Schu1, Takay, Torra, Wagne). Compounds in parentheses are not on the figure, but are reported by other workers. The existence of a narrow range of solid solution was reported (Panso), and then argued against (Wagne) by the same group.
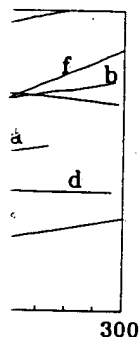
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:ansition of $BiSrCaCuO_{7-\delta}$ (a)
: 901°C, (d) aluminum-doped
'pper-rich sample calcined at
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as the end-point oxides
stable at 950°, (Ba_3CuO_4),
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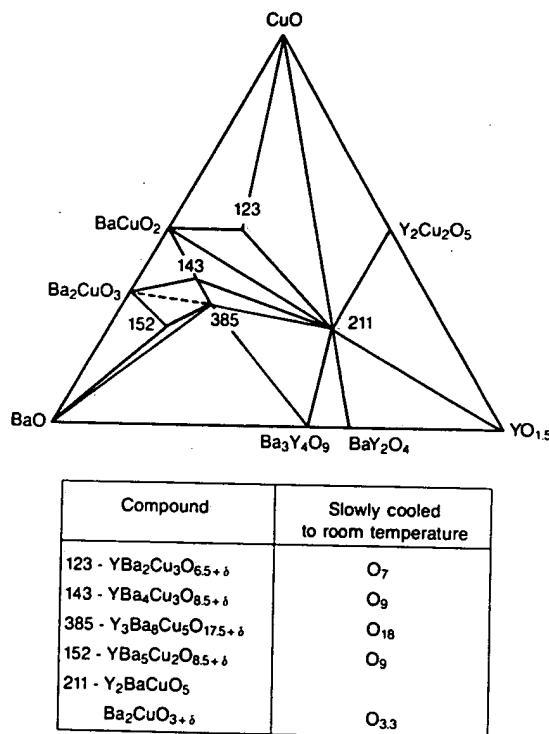:d by other workers. The
oorted (Panso), and then

Compound	Slowly cooled to room temperature
123 - $YBa_2Cu_3O_{6.5+\delta}$	O_7
143 - $YBa_4Cu_3O_{8.5+\delta}$	O_9
385 - $Y_3Ba_8Cu_5O_{17.5+\delta}$	O_{18}
152 - $YBa_5Cu_2O_{8.5+\delta}$	O_9
211 - Y_2BaCuO_5	
$Ba_2CuO_{3+\delta}$	$O_{3.3}$

Fig. V-2. Ternary phase diagram of the Y_2O_3–BaO–CuO system at 950°C. The green phase [Y_2BaCuO_5, (211)] the superconducting phase [$YBa_2Cu_3O_{7-\delta}$, (123)], and three other compounds are shown in the interior of the diagram (DeLee).

B. METHODS OF PREPARATION

In this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol–gel techniques (Hatfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical processes involved in the transformation of a mixture of compounds into a superconductor. The coprecipitation technique mixes the constituents on an atomic scale and forms fine powders, but it requires careful control of the pH and some familiarity with analytical chemistry. The sol–gel procedure requires more competence in analytical procedures.

In the solid-state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates, or carbonates of Ba, Bi, La, Sr, Tl, Y, or other elements. Sometimes nitrates are formed first by dissolving oxides in nitric acid and decomposing the solution at 500°C before calcination

(e.g., Davis, Holla, Kelle). These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcining for an extended period (≈ 20 hr) at elevated temperatures ($\approx 900°C$). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step. As the reaction proceeds, the color of the charge changes. The process usually ends with a final oxygen anneal followed by a slow cool down to room temperature of the powder, or pellets made from the powder, by sintering in a cold or hot press. Sintering is not essential for the chemical process, but for transport and other measurements it is convenient to have the material pelletized. A number of researchers have provided information on this solid-state reaction approach (e.g., Allge, Finez, Galla, Garla, Gopal, Gubse, Hajk1, Hatan, Herrm, Hika1, Hirab, Jayar, Maen1, Mood1, Mood2, Neume, Poepp, Polle, Qadri, Rhyne, Ruzic, Saito, Sait1, Sawa1, Shamo, Takit, Tothz, Wuzz3).

Some of the earlier works on foils, thick films, wires, or coatings employed a suspension of the calcined powder in a suitable organic binder, and the desired product was obtained by conventional industrial processes such as extruding, spraying, or coating.

In the second or coprecipitation process the starting materials for calcination are produced by precipitating them together from solution (e.g., Asela, Bedno, Leez7, Wang2). This has the advantage of mixing the constituents on an atomic scale. In addition the precipitates may form fine powders whose uniformity can be controlled, which can eliminate some of the labor. Once the precipitate has been dried, calcining can begin as in the solid-state reaction procedure. A disadvantage of this method, at least as far as the average physicist or materials scientist is concerned, is that it requires considerable skill in chemical procedures.

Another procedure for obtaining the start-up powder is the sol–gel technique in which an aqueous solution containing the proper ratios of Ba, Cu, and Y nitrates is emulsified in an organic phase and the resulting droplets are gelled by the addition of a high-molecular-weight primary amine which extracts the nitric acid. This process was initially applied to the La materials, but has been perfected for YBaCuO as well (Cimaz, Hatfi).

When using commercial chemical supplies to facilitate the calcination process a dry or wet (acetone) pregrinding with an agate mortar and pestle or a ball mill is recommended. Gravimetric amounts of the powdered precursor materials are thoroughly mixed and placed in a platinum or ceramic crucible. Care must be taken to ensure the compatibility of the ceramic crucible with the chemicals to obviate reaction and corrosion problems.

Complete recipes for the YBa* material have been described (e.g., Gran2). Typically, the mixture of unreacted oxides is calcined in air or oxygen around 900°C for 15 hr. During this time the YBaCuO mixture changes color from the green Y_2BaCuO_5 phase to the dark gray $YBa_2Cu_3O_{7-\delta}$ compound. Then the charge is taken out, crushed, and scanned with X rays to determine its purity. If warranted by the powder pattern X-ray scan, the calcination process is repeated. Often, at this stage the material is very oxygen poor, and electrically it is semi-

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